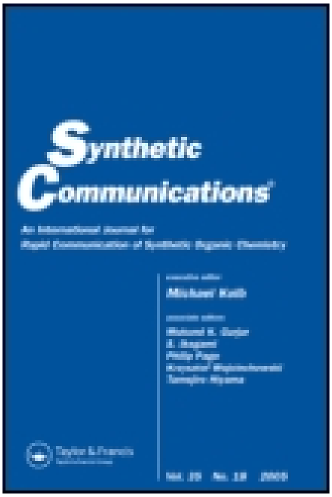

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Synthesis of New Diethynylbenzene Derivatives

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ABSTRACT

The preparation of new monomeric diacetylenic aromatic compounds is described.

INTRODUCTION

Diacetylenes have been the object of great interest and extended research, because upon polymerization they can give rise to extended conjugated π-systems. A number of different polymers can be obtained from the polymerization of diacetylene monomers, depending on the relative position of

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the two triple bonds in the monomer. The resulting polyacetylenes have physical and chemical properties[1] that make them interesting materials for use in electronics, optics, biophysics,[2] biochemistry, and time-temperature devices.[3]

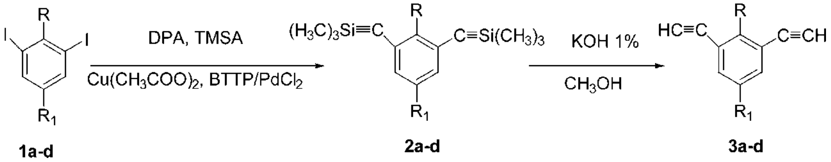
Diethynylbenzene derivatives could be considered important monomers in the synthesis of potentially conducting polymers. Knowing that the electric conductivity of polymers depends on the nature of the substituents of the benzene ring, it is interesting to synthesize diethynylbenzene derivatives in order to study the substituent effect on the characteristics of the polymer.

For these reasons, following our interest in the preparation and characterization of potentially conducting polymers related to polydiethynyl benzenes,[4−7] we report, here, the preparation of the new monomeric diacetylenic aromatic compounds, **3a–d**, bearing different substituents, which can be used as precursors of polymers and which are, moreover, of interest in their own right as unusual ethynylated compounds.

The diethynylbenzene derivatives (**3a–d**) were synthesized as depicted in Sch. 1 using Pd/Cu-catalyzed coupling of a silylating agent with an aryl iodide according to a similar procedure by Horn et al.[8] We have chosen the (trimethylsilyl)acetylene as silylating agent, because it can be quantitatively removed by treatment with dilute alkali.

The trimethylsilyl-protected ethynyl aromatics (**2a–d**) are very stable intermediates, and it has been possible to isolate and characterize them in this work. The mass fragmentation pattern of intermediates, **2a–d**, whose analytical data are reported in Table 1, together with those of compounds **1c** and **3a–d**, supports the assigned structures: they generally exhibit an intense molecular ion (100%) and a characteristic fragmentation ion at M-15 corresponding to a methyl group loss. Compounds **2a** and **3a** have been reported previously,[9] but no data have been published.

A mild basic hydrolysis of intermediates **2a–d** is sufficient to remove the TMS group affording diethynyl derivatives **3a–d**, whose mass spectra show an intense molecular ion (100%).



Scheme 1.

Table 1. Analytical and chemical-physical data of compounds **1c**, **2a–d**, and **3a–d**.

				Found (calcd.) (%)		
Compound	Yield (%)	M.p. (°C)	Molecular formula	C	H	N
1c	45	95–97[11] (102)	$C_6H_5I_2N$	20.97 (20.89)	1.47 (1.46)	4.07 (4.06)
2a	60	55–57	$C_{16}H_{21}NO_2Si_2$	61.15 (60.91)	6.74 (6.71)	4.46 (4.44)
2b	40	146–148	$C_{16}H_{21}NO_3Si_2$	67.53 (67.30)	8.14 (8.12)	4.92 (4.91)
2c	68	62–64	$C_{16}H_{23}NSi_2$	58.13 (57.97)	6.36 (6.38)	4.22 (4.23)
2d	45	203–205	$C_{16}H_{22}N_2O_2Si_2$	58.31 (58.14)	6.69 (6.71)	8.45 (8.48)
3a	85	119–121	$C_{10}H_5NO_2$	70.39 (70.18)	2.95 (2.94)	8.20 (8.18)
3b	70	118–121	$C_{10}H_5NO_3$	85.42 (85.08)	5.01 (5.00)	9.95 (9.92)
3c	80	125–127	$C_{10}H_7N$	63.92 (64.18)	2.70 (2.69)	7.46 (7.48)
3d	78	213–214	$C_{10}H_6N_2O_2$	64.29 (64.52)	3.23 (3.25)	14.99 (15.05)

EXPERIMENTAL

Melting points were obtained on a Büchi 510 Melting Point Apparatus and are uncorrected. Analytical TLCs were run on commercial Merck plates coated with silica gel G/UV 254 nm (0.20-mm thick).The ^{1}H-NMR spectra were recorded on a Bruker AM-400 (400 MHz) FT spectrometer and the chemical shifts were reported in ppm referring to the solvent peak. The IR spectra were performed on a Perkin–Elmer 1605 FT spectrophotometer on potassium bromide mulls. The electron impact mass spectral data were obtained with a Saturn 2000 GC/MS using a CP-SIL5 CB Low Bleed/MS 30 m, 0.25 ID column and EI at 70 eV. Elemental analyses for C, H, and N were performed on a Carlo Erba model 1106 elemental analyzer, and the analytical results were within $\pm 0.4\%$ of the theoretical values.

Unless otherwise specified, all reagents and solvents were obtained from Aldrich Chemical, and were used without any further purification.

The 3,5-diiodonitrobenzene **1a**, which is not commercially available, was prepared according to the literature.[10] The 3,5-diiodoaniline **1c** was obtained by catalytic hydrogenation of **1a** in EtOH at 15°C using Raney-Nickel as catalyst.[11] Commercial 2,6-diiodo-4-nitrophenol **1b** and 2,6-diiodo-4-nitroaniline **1d** were purified with acetone, acetic acid, and diethylether, and then filtered as yellow crystals m.p. 251–253°C and 155–157°C, respectively. Bis(Triphenylphosphine)palladium(II)chloride was purified by crystallization from chloroform. Diisopropylamine was freshly distilled.

General Procedure for the Synthesis of *bis*(Trimethylsilyl)-Ethynyl Derivatives 2a–d

bis(Triphenylphosphine)palladium(II)dichloride (BTPP/$PdCl_2$) (0.35 g, 0.49 mmol) and copper(II)acetate (0.1 g, 0.50 mmol) were added to a solution of **1a–d** (0.020 mmol) in 50 mL of diisopropylamine. The solution was degassed by flowing nitrogen through it, and then 3.1 mL (21.93 mmol) of (trimethylsilyl)acetylene (TMSA) was added. The solution was kept under stirring at room temperature for 1 hr. The solution was then filtered to remove the precipitate of diisopropylamine hydroiodide salts, and the solvent was removed under reduced pressure. The crude residue was dissolved in dichloromethane, extracted first with 5% HCl solution, then with water, and dried to give the Bis(trimethylsilyl)-ethynyl derivatives **2a–d** after distillation of the solvent. Compounds **2a–d** were purified by column chromatography (silica gel, hexanes : diethylether 20 : 1 as eluent) and crystallized from ethanol.

2a. ^{1}H-NMR (CD_3COCD_3): $\delta = 8.54$ (s, 2H, Ar-H), 8.30 (s, 1H, Ar-H), 0.26 (s, 18H, $6CH_3$). ^{13}C-NMR: $\delta = 147.6$ (C-1), 141.8 (C-4), 126.9 (C-2 and C-6), 122.8 (C-3 and C-5), 85.0 (C$\equiv$), 78.0 ($\equiv$C$-$Si), -1.0 (CH_3).

2b. ^{1}H-NMR (CD_2Cl_2): $\delta = 8.16$ (s, 2H, Ar-H), 4.30 (s, broad, 1H, OH, D_2O exch.), 0.26 (s, 18H, $6CH_3$). ^{13}C-NMR: $\delta = 170.2$ (C-1), 140.2 (C-4), 128.3 (C-3 and C-5), 110.0 (C-2 and C-6), 85.0 (C$\equiv$), 78.0 ($\equiv$C$-$Si), -1.0 (CH_3).

2c. ^{1}H-NMR (CD_3COCD_3): $\delta = 7.15$ (s, 2H, Ar-H), 6.56 (s, 1H, Ar-H), 3.60 (s, broad, 2H, NH_2, D_2O exch.), 0.26 (s, 18H, $6CH_3$). ^{13}C-NMR: $\delta = 153.9$ (C-1), 132.6 (C-3 and C-5), 117.7 (C-4), 108.5 (C-2 and C-6), 85.0 (C$\equiv$), 78.0 ($\equiv$C$-$Si), -1.0 (CH_3).

2d. ^{1}H-NMR (CD_3COCD_3): $\delta = 8.12$ (s, 2H, Ar-H), 5.50 (s, broad, 2H, NH_2, D_2O exch.), 0.26 (s, 18H, $6CH_3$). ^{13}C-NMR: $\delta = 160.0$ (C-1), 137.6 (C-4), 127.7 (C-3 and C-5), 109.4 (C-2 and C-6), 85.0 (C$\equiv$), 78.0 ($\equiv$C$-$Si), -1.0 (CH_3).

General Procedure for the Synthesis of Diethynylbenzene Derivatives 3a–d

An excess of 1% KOH solution was added to a solution of *bis*(trimethylsilyl)-ethynyl derivatives **2a–d** (mmol) in 80 mL of methanol to remove the trimethylsilyl groups. After 20 min, the volume of the resulting solution was reduced, diluted with water, extracted with chloroform, and dried over sodium sulfate. After distillation of the solvent, the crude solid was column chromatographed (silica gel, diisopropylether : hexanes 2 : 1 as eluent) and crystallized from benzene to give the pure diethynyl derivatives **3a–d**.

3a. ^{1}H-NMR (CD_3COCD_3): $\delta = 8.33$ (s, 2H, Ar-H), 7.97 (s, 1H, Ar-H), 4.23 (s, 2H, 2CH). ^{13}C-NMR: $\delta = 147.6$ (C-1), 141.8 (C-4), 126.9 (C-2 and C-6), 122.8 (C-3 and C-5), 84.6 (C$\equiv$), 78.3 ($\equiv$CH); GC-MS: $m/z = 171$ [M^+]; 155 [$M^+ - O$]; 141 [$M^+ - NO$]; 125 [$M^+ - NO_2$].

3b. ^{1}H-NMR (CD_2Cl_2): $\delta = 8.52$ (s, 2H, Ar-H), 6.30 (s, broad, 1H, OH, D_2O exch.), 3.06 (s, 2H, 2CH). ^{13}C-NMR: $\delta = 170.6$ (C-1), 140.2 (C-4), 128.3 (C-3 and C-5), 110.0 (C-2 and C-6), 84.6 (C$\equiv$), 78.3 ($\equiv$CH). GC-MS: $m/z = 187$ [M^+]; 171 [$M^+ - O$]; 157 [$M^+ - NO$]; 141 [$M^+ - NO_2$].

3c. ^{1}H-NMR (CD_3COCD_3): $\delta = 7.15$ (s, 2H, Ar-H), 6.56 (s, 1H, Ar-H), 4.70 (s, broad, 2H, NH_2, D_2O exch.), 4.23 (s, 2H, 2CH). ^{13}C-NMR: $\delta = 153.9$ (C-1), 132.6 (C-3 and C-5), 117.7 (C-4), 108.5 (C-2 and C-6), 84.6 (C$\equiv$), 78.3 ($\equiv$CH). GC-MS: $m/z = 141$ [M^+]; 114 [$M^+ - HCN$].

3d. ^{1}H-NMR (CD_3COCD_3): $\delta = 8.08$ (s, 2H, Ar-H), 6.78 (s, broad, 2H, NH_2, D_2O exch.), 4.67 (s, 2H, 2CH). ^{13}C-NMR: $\delta = 160.0$ (C-1), 137.6 (C-4), 127.7 (C-3 and C-5), 109.4 (C-2 and C-6), 84.6 (C$\equiv$), 78.3 ($\equiv$CH). GC-MS: $m/z = 186$ [M^+]; 170 [$M^+ - O$]; 156 [$M^+ - NO$]; 140 [$M^+ - NO_2$].

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